

VII. *On the Thickness and Electrical Resistance of Thin Liquid Films.*

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IN a paper on the “Limiting Thickness of Liquid Films,” presented to the Royal Society in 1883,* we proved that in the case of a large number of films the mean thickness of that part which was thin enough to display the black of the first order of NEWTON’S rings was $11\cdot6\ \mu.\mu.$ (micromillimetres).

The validity of the methods employed was assured by the agreement between the results obtained. The mean thickness of a number of black films was measured optically by a method which involved the assumption that the refractive index of the substance of the film was the same as that of a large mass of the same liquid. The thickness of black films was also determined by measuring their electrical resistances, and assuming that the specific resistance was the same as that of the liquid in mass. The means of the results obtained by the two methods were $11\cdot8\ \mu.\mu.$ and $11\cdot3\ \mu.\mu.$ respectively, which were sufficiently in accord to justify the assumptions.

While, however, there was this close agreement in the mean results, the numbers obtained by different experiments differed rather widely. We then expressed the opinion that “the differences between the numbers given by the optical method are, perhaps, not much in excess of the probable error of experiment, but in the case of the electrical observations they far exceeded it.”† We then proceeded, in a passage which it is perhaps unnecessary to quote at length, to give reasons for our belief that “the thickness of the black portions is really different in different films,” and added that “into the cause of the variations in the thickness of different black films we do not now propose to enquire.” Since that date we have made a large number of new experiments in which the thicknesses of black films of different composition have been determined both by electrical and optical methods. Some of the observations were described to the Society in a paper “On Black Soap Films,” which was read on March 1, 1890. The main object then before us was to enquire whether the rate of formation of the black depends on its thickness. Before the paper was published, fresh facts came to our knowledge which appeared to show that however this might be, there was an undoubted and much more clearly marked relation between the com-

* ‘Phil. Trans.’ 1883, Part 2, p. 645.

† *Loc. cit.*, p. 660.

position of the film and the thickness of the black which it produces. We therefore requested that the publication of our paper might be delayed, and we now include the results then obtained in an account of further experiments which have been carried out as opportunity offered during the last three years.

We think that it will be most convenient to state our results in a series of propositions, and to describe in each case the experimental evidence on which the conclusions are based. It is necessary to state, by way of preface, that the optical and electrical methods of measuring the thickness of the films are in all essentials identical with those described in our paper "On the Limiting Thickness of Liquid Films," already referred to, and that the precautions therein detailed have been carefully attended to.

Proposition I.—In the case of soap films formed with a solution of oleate of soda (one part of oleate in about 70 of water) containing about 3 per cent. of potassium nitrate, the mean thickness when they are thin enough to appear black, is the same whether measured optically or electrically, and is about 12.1 $\mu\mu$.

The proof of this proposition is contained in our paper on the limiting thickness of liquid films already referred to.

It will, perhaps, be remembered that a similar statement is also true when the solution is mixed with two-thirds of its volume of PRICE's glycerine.

In the next two propositions we deal exclusively with results obtained by the optical method of measuring the thickness of the films.

Proposition II.—If the proportion of potassium nitrate mingled with the solution be diminished the thickness of the film as measured by the optical method increases.

This is proved by the following Table. In all cases oleate of soda was used, the proportion being 1 part of soap to 50 of water in the case of the first two liquids, and 1 of soap to 40 of water in the last two. These variations in the proportion of soap to water were made from time to time in consequence of the great difficulty of getting black films at all. Often an entire day was devoted to the work without a single result being obtained. It thus became necessary to try a new solution, which was purposely made a little different from the old one, in the hope of securing some black films on which measurements could be made. Even had we been aware, at the time when many of these experiments were carried out, of the effect on the thickness of the film of a change in the proportion of soap, we could hardly have made all the experiments under precisely similar conditions. The question as to why a particular solution sometimes does and sometimes does not readily thin to the black cannot at present be answered, and it is only by varying the conditions that any results can be obtained.

In the Table the results of the individual experiments are given, each thickness being the mean of the thicknesses of about 100 films.

TABLE I.

Percentage of KNO_3 .	Thickness of black films in $\mu.\mu.$, measured optically.	Mean.
3.0	12.6, 12.2, 12.3	12.4
1.0	15.7, 11.4, 13.7, 13.2	13.5
0.5	13.4, 15.7	14.5
0.0	23.2, 22.3, 20.3, 22.8	22.1

It is satisfactory to note the close agreement of the above thickness for the 3 per cent. solution with that previously obtained by us ('Limiting Thickness,' *loc. cit.*, p. 661), the numbers being 12.4 and 12.1 $\mu.\mu.$ respectively. We may note, however, that the solution previously used contained less soap (*viz.*, 1 in 70 instead of 1 in 50), a point to which we shall refer again.

The number of observations is hardly sufficient, and the discrepancies between the individual measures on 1 per cent. and 0.5 per cent. solutions are too great to warrant our insisting on the gradual increase in the thickness at these percentages. There can, however, be no possible doubt that when no KNO_3 is present, the numbers are much larger than when the solution contains 3 per cent. of the salt.

This result is confirmed by the following measurements in which soft soap (oleate of potash) was used instead of oleate of soda, and sodium sulphate instead of potassium nitrate. The solution became thick when a larger proportion than one per cent. of Na_2SO_4 was mingled with it.

TABLE II.—Soft soap ; 1 part in 40 of water.

Percentage of Na_2SO_4 .	Thickness of black films in $\mu.\mu.$, measured optically.	Mean.
1.0	14.1, 16.3, 14.3	14.9
0.0	20.1, 18.2, 19.8, 21.3, 17.8, 19.7	19.5

A further confirmation is obtained by the use of *liquide glycérique*. It is practically impossible to employ a soap solution in which more than 3 per cent. of potassium nitrate has been dissolved, as the liquid becomes "ropy" and does not thin to the black. With a *liquide glycérique*, however, containing two parts by volume of glycerine to three of soap solution, the proportion of potassium nitrate can be largely

increased. The following Table (Table III.), exhibits the results obtained. We follow the plan which we have adopted in previous papers of calculating the percentage of KNO_3 with reference to the soap solution only. Thus, if equal volumes of the two liquids were compared, a 10 per cent. *liquide glycérique* would contain the same amount of KNO_3 as a 6 per cent. solution of soap in water only, the proportion of salt to soap being the same in each case.

TABLE III.—*Liquide Glycérique*; 1 part of soap to 40 of water in all cases.

Date.	Percentage of KNO_3 .	Thickness in $\mu., measured optically.$	Mean.
1891	8.66	8.3, 9.7, 9.4, 10.5	9.5
"	5.2	{ 10.7, 11.0, 10.6 } { 11.8, 11.2, 11.2 }	11.1
1883	3.0	{ 10.6, 10.2, 12.5, 10.7 } { 10.2, 11.0, 9.4 }	10.7
1891	0.0	23.9, 25.4	24.7

These figures are, we think, sufficient to prove the truth of the proposition.

We now pass from a study of the effect of a change in the proportion of salt to that of an alteration in the quantity of soap dissolved, the optical method of measuring the thickness being still adhered to.

Proposition III.—If the proportion of oleate of soda in a solution containing no potassium nitrate be diminished, the thickness of the film, as measured by the optical method, increases.

TABLE IV.—Hard Soap. No dissolved Salt.

Proportion of soap to water.	Thickness of black film in $\mu., measured optically.$	Mean.
1 to 30	21.8, 21.7, 21.0, 22.0	21.6
1 „ 40	23.2, 22.3, 20.3, 22.8	22.1
1 „ 60	28.1, 27.4, 27.6	27.7
1 „ 80	28.8, 29.4, 29.8	29.3

The first point to notice is that the results given in this Table strengthen the argument in favour of Proposition II. One part of soap was used with 50 of water in the two solutions first referred to in Table I., but in the case of the last two the proportion was 1 to 40. The above Table proves that, had the proportion of soap been the same in all cases, the relative thickness of the films formed with a solution containing no KNO_3 would have been even greater than appears from Table I. It is,

therefore, not too much to say that the average thickness, measured optically, of a black soap film formed of a solution of 1 part soap in 50 of water, but containing no KNO_3 , is double that of a similar film made of a solution of the same composition in which 3 per cent. of KNO_3 has been dissolved.

The results obtained with the plain hard soap solution are confirmed by experiments on *liquide glycérique*.

TABLE V.—*Liquide glycérique*. No Salt dissolved.

Proportion of soap to water.	Thickness of black film in $\mu\mu$., measured optically.	Mean.
1 to 40	23.9, 25.4	24.6
1 „ 60	28.6, 30.0, 32.7, 27.9	29.8

In this case, again, a decrease in the proportion of soap produces an increase in the apparent thickness of the black.

When the solution contains 3 per cent. of KNO_3 , variation in the proportion of dissolved soap has comparatively little influence on the thickness of a black film. This statement is justified by the figures given in Table VI.

TABLE VI.—Hard Soap. 3 per cent. of KNO_3 .

Proportion of soap to water.	Mean thickness of black in $\mu\mu$., measured optically.	Greatest and least values.	Date.
1 in 40	13.0	13.5–12.7	April, 1891
1 „ 50	12.1	12.9–11.6	„ „
1 „ 60	11.55	Single observation	July, 1892
1 „ 70	12.1	14.4–10.3	1883

The question now arises whether the large increase in the thickness of black films, formed from what we may, perhaps, for convenience, call an *unsalted* solution is real, or whether it is due to some incorrect assumption. The only point where error is possible is in the hypothesis that the refractive index is the same as in the liquid in mass. The thickness of the film varies inversely as $n - 1$ (n being the refractive index), and as the refractive index of the soap solution is about 1.34, it would have to be reduced to about 1.17 in order that the calculated thickness might be doubled. It appears, therefore, *à priori*, extremely improbable that the mere addition of 3 per cent. of KNO_3 should so completely change the optical properties of the liquid that, whereas, if the salt be added, the refractive index is practically the same in thin films and in the liquid in mass, as is proved both by our experiments of 1883

and by many made subsequently (see Tables I. and VI.); yet, without the salt, the refractive index of the film should be as much as 13 per cent. less than that of the liquid in mass.

To this *a priori* argument the following may be added. During the progress of our work a paper has appeared by Herr DRUDE ('Wied. Ann.,' vol. 43, 1891, p. 169), in which the author, using an experimental method totally different from that employed by us, compares the refractive indices of black and coloured soap films, of which the latter may unquestionably be taken as nearly the same as if not absolutely identical with that of the liquid in mass. Using solutions both with and without the addition of a salt (viz., Na_2SO_4), the author finds that the refractive indices of the black and coloured films do not differ by more than about 1 part in 140. Such a variation, if satisfactorily established, would only affect the apparent thickness of the films as measured by the optical method by 2.6 per cent., whereas, according to the measurements given above, the presence or absence of the salt alters the apparent thickness by 100 per cent.

On the whole, then, we certainly think that the differences of thickness indicated by the optical method of measurement may be relied upon as being not merely apparent but real, and we shall hereafter treat this point as established.

Having thus studied the effect of the composition of the films on their thickness, we proceed to describe the results of observations in which the apparent thickness was measured by the electrical method.

Proposition IV.—*If the proportion of potassium nitrate mingled with the solution be diminished, the thickness of a black film, as measured by the electrical method, increases, but in a far larger ratio than would be inferred from the optical method. If the proportion of salt be diminished to zero the thicknesses thus calculated are greater than the greatest thickness at which a film can appear black. In such cases, therefore, the electrical method does not give the true thickness of the film, and the hypothesis that the specific conductivities of the film and of the liquid in mass are identical is untenable.*

This statement is proved by the following table. A very large number of observations have been made with unsalted solutions, but we give the results of the latest experiments only which were made with all the precautions which experience has shown to be necessary.

TABLE VII.—Hard Soap ; 1 part to 70 of water.

Percentage of KNO_3 .	Thickness in $\mu\mu$, measured electrically.	Mean.
3	9.6, 11.6, 12.3, 7.7, 10.0, 12.5	10.6
2	12.3, 20.0, 8.3, 10.7, 10.5, 11.3, 11.1, 17.3	12.7
1	20.1, 28.0, 22.1, 30.3, 21.6	24.4
0.5	29.8, 29.8, 25.2, 25.8, 22.0, 26.4, 26.4	26.5
0.0	146, 103, 139, 215, 197, 240, 134.98, 149, 155, 129, 79, 118, 167	148
0.0*	156, 84, 213, 240, 159, 250	184

The first thing to notice with regard to this table is that when the solution contained 3 per cent. of KNO_3 , both the variations in the results of the individual experiments and the mean value of the thickness are in close agreement with the corresponding values obtained by us in 1883 ("Limiting Thickness," &c., *loc. cit.*, p. 661). This fact is proved by the following table, in which the thicknesses are as usual expressed in $\mu\mu$.

TABLE VIII.

Date.	Largest value.	Smallest value.	Mean of all values.
1882 . . .	14.5	7.2	11.7
1891 . . .	12.5	7.7	10.6

Next we note that in Table VII. the indications of an increase in the calculated thickness are unmistakable when the quantity of dissolved salt is reduced to 1 per cent. When no salt is used, and the proportion of soap to water is as 1 to 40, the mean thickness is in one case no less than 184 $\mu\mu$. The colour corresponding approximately to this would be the beginning of the yellow or of the red of the first order, according as the incidence of the light was grazing or normal.

Under no possible circumstances could a film of this thickness appear black. The beginning of the black, according to NEWTON, occurs when the thickness is 36 $\mu\mu$, which is only about one-fourth or one-fifth of the mean value obtained for unsalted solutions. We are therefore driven to the conclusion that the close agreement between the results of the optical and electrical measures of the thickness of black

* One part of soap to 40 of water.

films obtained both in 1883 and in 1890-92, when the solution contained 3 per cent. of KNO_3 , does not hold in the case of unsalted solutions. We have already stated that we believe the optically measured thicknesses to be correct mean values in all cases, but, whether this is so or not, the electrically measured values cannot for the reasons just given be real thicknesses. There must, therefore, when no metallic salt is present, be a difference between the specific conductivities of a film and the liquid of which it is formed.

This conclusion is borne out by the results of experiments made with soft soap.

The following table contains the results of measurements on 23 films made in the summer of 1889.

TABLE IX.—Soft soap. No salt dissolved.

Thickness in $\mu.\mu.$ as given by the electrical method.				
169,	166,	185,	171,	189,
173,	120,	126,	150,	151,
150,	145,	142,	143,	148,
150,	188,	80,	157,	165,
179,	252,	232,		
Mean 162.				

Proposition V.—The apparent thickness, as measured by the electrical method, of different black films formed of an unsalted solution is very variable. In some cases, at all events, this is due to a real variation in thickness.

The results given above are sufficient proof of the apparent variability of the thickness of the film.

The best proof that this variability is sometimes real, is the fact that we have distinctly seen two different shades of black in the same film. NEWTON recognised two different intensities of black in soap bubbles, and Lord KELVIN has on more than one occasion asked us whether we have noticed the same phenomenon. So long as our experiments were made with a solution containing a relatively large proportion of salt our answer was always in the negative. Since we have been working with solutions which contain but little salt, we have occasionally noticed traces of two different black tints in films containing not more than one per cent. of KNO_3 . In films containing no salt the phenomenon is of frequent occurrence. The difference of tint is but slight and may easily be overlooked, but in many cases a definite line of demarcation can be observed between the two tints, so that we can certainly state that the upper part of the film showed one tint and the lower part the other, which may be distinguished as β_1 and β_2 respectively. The line of separation is very irregular in form. That which divides the black and coloured parts of the cylindrical

films we employ is almost always a horizontal circle. This is by no means the case with the boundary between the two black tints. Sometimes one completely encloses a patch of the other, sometimes the line of separation is sinuous or stands higher at one part of the film than at another. In some cases when no difference of hue was observed, the passage of an electrical current through the film either created the difference or enabled us to notice a boundary line which we had not before perceived. It is a very curious fact that under such circumstances tiny white flecks appear in the black along the boundary line between the two tints. Sometimes this line has been observed before the passage of the current, sometimes it has not been noticed until the flecks have drawn attention to its existence.

These eye observations are confirmed by electrical measurements. It is indeed only on one fortunate occasion that we have been able to measure electrically the apparent thicknesses corresponding to the two black tints when exhibited by the same film. Both hues were then seen and the line of demarcation was above the upper needle. The thickness (measured electrically) of the part between the needles was $200\ \mu.\mu.$ When the line of separation was about half-way between the two needles, the thickness (assumed uniform throughout, and, therefore, really the mean thickness of the two parts) was $157\ \mu.\mu.$ When the line had reached the lower needle, so that both needles had passed through the upper black region, the thickness was $116\ \mu.\mu.$ In this film the curve of separation was approximately a horizontal circle, so that when the needles were in the upper or lower black region the whole of the corresponding horizontal ring on the cylinder was of the same hue. In a few other cases we have seen the line of demarcation pass the upper needle, and as it sank, the apparent thickness of the film, as measured electrically, invariably diminished. In one case we obtained a measurement when the two needles were in β_1 the apparent thickness was $110\ \mu.\mu.$, which, as will be seen by comparing the results for unsalted solutions in Table VII. and IX. is relatively small, but agrees with the value $116\ \mu.\mu.$ obtained on the occasion already described. Unfortunately on this occasion no measure could be made on β_2 .

The value of the confirmation—given by the variation of the electrical measures made upon the same film—of the fact disclosed by eye observation that, in an unsalted film there are discontinuous thicknesses, both of which are black, is enhanced by comparison with the extreme constancy of electrical measures which we have previously obtained with salted solutions, provided only that they were made upon the same film.

When experimenting with salted solutions we have failed ("Limiting Thickness, &c.," *loc. cit.*, p. 652) to detect any change in the thickness of the black part of a film which lasted for more than two hours.

These observations certainly suggest that even in cases where we have not noticed a line of separation, which is the only optical indication of the discontinuity of the black part of the film which our methods allow, the extreme variability in the

electrically measured thicknesses is to be accounted for by the gradual substitution of one black tint for the other. The line, as we have said, is difficult to see. It is quite probable that the white flecks which draw attention to it are more numerous on some occasions than on others, or may sometimes be altogether absent, and thus the fact that no line has been seen does not prove that the black film was not really divided into the two parts of different thicknesses. It will be observed, however, that we have so framed the proposition under discussion that the possible agency of other causes in bringing about changes in the electrically measured thickness is not denied.

Proposition VI.—Whereas the specific conductivity of black films formed of solutions containing about 3 per cent. of KNO_3 is approximately the same as that of the liquid in mass, the specific conductivity of similar films formed of solutions containing no KNO_3 , but consisting of a solution of oleate of soda or oleate of potash in water is very different from that of the liquid in mass.

This is merely a deduction from our previous work and from Propositions III. and IV.

If the optical and electrical methods give the same result, it may be inferred that the specific resistance is not affected by the tenuity of the film. Hence, since this is the case for films which contain considerable proportions of salt, the first part of the proposition is true. If the results obtained by the optical and electrical methods are at variance, one of the assumptions made (viz., that the refractive index and the specific conductivity are independent of the thickness) is incorrect. We have already shown that the change is too great to be accounted for by a variation in the refractive index. We are, therefore, driven to attribute the anomalous, or rather impossible, values of the thickness of unsalted films, obtained by the electrical method, to a change in the specific conductivity.

Proposition VII.—The change in specific conductivity—

- (1.) *Is independent of moderate changes of temperature ;*
- (2.) *Is not due to the absorption or evaporation of water by the film ;*
- (3.) *Is not due to a change in the composition of the liquid by electrolytic decomposition produced by the current used to measure the resistance of the film ;*
- (4.) *Is not affected by a very large change in the quantity of carbonic acid in the air around the film.*

(1.) The first of these statements is proved by such facts as the following. The value of β (the apparent thickness of the black) was, on one occasion, 139 $\mu\mu$. when

the temperature was $22^{\circ}2$ C. The same liquid on the same day gave $\beta = 103 \mu.\mu.$ at 18° , and, in the case of another film, $\beta = 147 \mu.\mu.$ at 18° . In this case the variations of β , when the temperature was constant, were greater than the change which might otherwise have been attributed to a rise of 4° in temperature. Sometimes the larger value was found at the lower temperature. Thus, in one case, when

$$\begin{array}{ll} t = 26^{\circ}3 & \beta = 135 \mu.\mu. \\ t = 21^{\circ}0 & \beta = 237 \mu.\mu. \end{array}$$

Sometimes precisely the reverse result was obtained, as

$$\begin{array}{ll} t = 21^{\circ}1 & \beta = 201 \mu.\mu. \\ t = 18^{\circ}7 & \beta = 171 \mu.\mu. \end{array}$$

Instances such as these might be multiplied indefinitely, and suffice to show that the relatively small variations of temperature which occurred during our experiments are not the cause of the fact that a film, of which the true thickness is about $22 \mu.\mu.$, appears when measured electrically to have a thickness of $184 \mu.\mu.$

(2.) The precautions taken to prevent absorption or evaporation by the films were precisely the same as those which our previously published results have shown to be efficient in the case of *liquide glycérique*, which is much more sensitive to changes of hygrometric state than solutions containing no glycerine.

The bottom of the vessel in which the films were formed was flooded with the liquid. A continuous roll of linen dipped into the liquid, and could be moved so that all portions in turn were moistened, thus exposing a large evaporating surface. A hair hygrometer was enclosed in the vessel. No observations were made until the index of the hygrometer ceased to move. A constant hygrometric state was thereafter maintained. In the case of liquids not containing glycerine, we found that the layer of liquid at the bottom of the vessel was sufficient for this purpose, as the results were the same, whether the roll of linen was or was not used. The vessel in which the films were made was surrounded by a tank of water, the object of which was to check variations of temperature. To assure ourselves that the measurements were not affected by the diffusion of water vapour, into the interior we made experiments when the tank was empty as well as when it was full, and obtained precisely the same results in the two cases. Hence, considerable variations in the hygrometric state of the air close to the vessel, and in the means taken to secure a constant hygrometric state within the vessel produced no effect on the results.

(3.) As, in order to assist in reducing the thickness of a film, we frequently use electric currents which, although they are very weak, pass for some time through the film and are relatively strong when it is thick, we thought it very important to prove that the change in specific conductivity is not due to the passage of the current. Comparative observations were therefore made, in some of which a current from a

battery of from fourteen to twenty-eight Leclanché cells was passed through the film from the moment of its formation, in others no current was used until the time for measurement arrived, and then it was produced by seven Leclanché cells only, and was applied intermittently so that the circuit was not completed unless an observation was actually in progress.

The following results were obtained with an unsalted oleate of potash solution. Each of the values of β was derived from a different film, and the number of cells indicated is in each case that employed to pass a continuous current from the first formation of the film. Of course in all cases a current was used at the moment of measurement.

TABLE X.

Number of cells.	β (apparent thickness of black film measured electrically).
0	150, 171, 148, 150
14	151, 145, 142
28	150, 157, 179

These numbers prove that the results were not affected by the strength or duration of the current which was passed through the film before the measurements were actually made.

These observations were supplemented by others in which the resistance of films could be compared by means of currents which were practically instantaneous. For this purpose the needles were connected with the terminals of the secondary of a Ruhmkorff coil, a ballistic galvanometer being included in the circuit.

The primary circuit could be completed or broken by an independent key. In experiments on different films the circuit was always completed for the first time when the black had descended to the same distance below the lower needle, so that the throw would be nearly inversely proportional to the resistance of the black film.

The deflections of the galvanometer were identical in two cases, in one of which a current from twenty cells had been passed through the film (formed of an unsalted hard soap solution) from the time of its formation, while in the other a film formed of the same liquid had not been subjected to any electrical action until the transient current used in the measurement was employed. It might possibly be urged in answer to this that we have no evidence that the thickness of the black was the same in each case—that we may have been dealing with β_1 in the one case and β_2 in the other. If this were so the equality of the throws could only be explained by the hypothesis that the product of the thickness and specific conductivity is the same for β_1 and β_2 , and this is inconsistent with the large change in resistance which the substitution of one for the other has been proved above to produce.

In fact the observations are perhaps open to criticism of a precisely opposite kind, viz., that in view of the irregularities in the value of β obtained by our ordinary method of measurement, it is strange that on this occasion we should have obtained the same result in the case of two consecutive films. Such coincidences were not uncommon; but the objection is, perhaps, best answered indirectly by comparing the throws in the case of salted and unsalted solutions, and thus determining whether the ratio of the computed apparent thicknesses is about the same when transient and continuous currents are used. This experiment we have performed. With a solution containing 3 per cent. of KNO_3 the throw was 19 divisions of the scale. With an unsalted solution when the black had descended to the same level the throw was 9.5 divisions. The specific resistances of the two liquids were 36 and 890 ohms per cubic centim. respectively. If r_1 and t_1 are the resistance and calculated thickness of the unsalted film, and ρ_1 is the specific resistance of the liquid of which it is formed; and if r_2 , t_2 , ρ_2 have similar meanings with respect to the salted film, we have the equation

$$\frac{t_1}{t_2} = \frac{\rho_1 r_2}{\rho_2 r_1},$$

or, remembering that the throws are inversely proportional to the resistances,

$$\frac{t_1}{t_2} = \frac{890}{36} \times \frac{9.5}{19} = 12.4.$$

But t_2 , the thickness of a salted film, is about 12 $\mu.\mu.$ Hence t_1 , the calculated apparent thickness of the unsalted film, = 149 $\mu.\mu.$ This number is intermediate between the largest and smallest of those obtained by the continuous current method and exhibited in Table VII, and does not differ very widely from the mean, which is about 160.

On the whole then the evidence clearly points to the conclusion that the passage of the current does not produce the change of specific conductivity under discussion.

(4.) Passing now to the question as to whether absorption of CO_2 from the air is the efficient cause, it must be remembered—and this remark applies also to the possibility of the results having been affected by evaporation or change of temperature—that all our observations are based on a comparison between two solutions which differ only in the addition to one of them of not more than 3 per cent. of KNO_3 , or 1 per cent. of Na_2SO_4 . If, therefore, the change in specific conductivity were ascribed to any one of these causes, it is not only necessary to assume that the cause was competent to produce the change, but that its efficiency was very greatly modified by the addition of the salt.

As it is difficult to argue from the results of experiments conducted on the liquid in mass to the behaviour of a film, and as it is probable that, if sufficient time were allowed, the amount of CO_2 absorbed by a liquid containing a substance such as

oleate of soda, upon which it acts, might be very considerable, we have tested the matter by direct experiment. A series of observations were made when the air which surrounded, and that which was used to blow the films had been carefully freed from CO_2 by passage through three tubes containing caustic alkali. As it would have been extremely inconvenient to have made the apparatus air-tight, a current of the purified air was passed through it continuously during the whole of the experiment. Although, therefore, the proportion of CO_2 in the air around the films was—if not absolutely *nil*—very much reduced below its normal value, the results as regards the electrical thickness were practically identical with those obtained when no such precautions were taken.

TABLE XI.

Date.	Proportion of oleate to water.	Electrical thickness of black in $\mu\mu$.			
		Highest.	Lowest.	Mean of all.	Number of films.
June and July, 1890	$\frac{1}{70}$	240	79	148	14
		Taken without any special precaution. Linen band not used.			
November and December, 1890 . .	$\frac{1}{70}$	243	73	154	7
		Linen band used. Films blown with air freed from CO_2 , but no continuous flow of purified air through the film box.			
July, 1891	$\frac{1}{40}$	250	84	184	6
		See Table VII. Every known precaution used. Continuous flow of air freed from CO_2 through the film box.			

Although the mean values differ somewhat, it will be observed that the highest and lowest values in each set are about the same. There is thus no indication that the presence or absence of CO_2 in the air surrounding the film has any marked influence on its electrical thickness. This argument against CO_2 being the cause of the high conductivity of the thin films is much strengthened if we consider the ratio of the electrical to the optical thicknesses, *i.e.*, the ratio of the specific conductivity of the film to that of the liquid in bulk. Dividing each of the electrical thicknesses in the above table by the corresponding optical thickness given in Table IV., we get the three values, 5.2, 5.4, 8.3. Hence the specific conductivity of the film was about 50 per cent. greater when every precaution was taken to exclude CO_2 than when no

such precaution was taken, which is certainly opposed to the theory that CO_2 is the efficient cause.

Proposition VIII.—The change in specific conductivity is practically unaltered if the films are formed in an atmosphere of oxygen.

When the films were formed in an atmosphere of either oxygen or nitrogen they did not thin in the normal way. The black was either not formed at all, or, if formed, was streaked with lines and flecks of other colours. An electrical measurement therefore only gave the mean apparent thickness of a non-uniform mass, from which the thickness of the black could not be deduced. When the film case was filled, and the film itself blown with purified oxygen, from which all traces of chlorine had been carefully removed, it was, however, possible to make observations when the thickness corresponded to the white of the first order. This colour changes so slowly as the film thins that no accurate estimate of the thickness can be based upon it. Alternate series of measurements were, however, made when the box was filled with air and oxygen respectively with the following results:—

TABLE XII.

Air purified from CO_2 .		Oxygen.		Air purified from CO_2 .	
Colour of the first order.	Electrical thickness in $\mu.\mu.$	Colour of the first order.	Electrical thickness in $\mu.\mu.$	Colour of the first order.	Electrical thickness in $\mu.\mu.$
Yellow	407	Yellowish-white . .	403	White	465 to 383
White	387	Grey to white . .	326		
White, full of black spots	346	Grey (with black specks) to grey	296	Grey to white . .	316
Grey	286	Grey (mixed with black spots) to white	245	Grey to white . .	296
„	261				
„	236				

It must be clearly understood that the estimates of colours of films as thin as these are very untrustworthy, but they are, we think, sufficient to prove that the phenomena are substantially identical in air and in oxygen.

The thickness corresponding to the white of the first order, as given in NEWTON'S table, is $97 \mu.\mu.$ Hence, in all cases, the electrical very much exceed the true thicknesses. The first two numbers in the case of oxygen (in Table XII.) correspond to colours given by thicknesses a little greater and less respectively than that which corresponds to the white. Taking the mean of these, and also the mean of the extreme thicknesses for which the film appeared white in the second air experiment, we get the following Table:—

TABLE XIII.

	Electrical thickness of white.	Ratio to true thickness.
Air	387	3.99
Oxygen	364	3.75
Air	424	4.37
Air (later experiments; see p. 522)	434	4.47

The ratio obtained when oxygen was used is less than in the other cases, but the difference is small when the uncertainty of the colour estimates is allowed for; and the agreement is, at all events, sufficiently close to prove that a very great increase in the quantity of oxygen in the neighbourhood of this film produces little or no change in the specific resistance.

The nitrogen used was produced by heating a mixture of ammonium chloride and potassium nitrite, and was passed through dilute sulphuric acid and caustic potash. Whatever the cause may have been, we found that in this gas the film did not thin regularly, so as to exhibit pure and unmixed colours. Estimates of the thickness were therefore impossible.

Before proceeding to discuss these results further, it may be well to ask whether the large changes in specific conductivity affect the black films only, or whether similar phenomena can be detected when the thickness is greater. On this point we have made numerous observations, which have led us to the following conclusion:—

Proposition IX.—The specific conductivity of a soap film increases as the thickness decreases, but this increase is less in the case of a film formed of a solution to which a salt has been added, and cannot be detected in the case of a “liquide glycérique” such as that we have employed.

To justify this statement we adduce the following facts which are only samples of the results of a large number of experiments. Perhaps the most convenient way of testing the constancy of the specific conductivity of a film is to calculate the thickness from observations on the electrical resistance, assuming that the specific resistance is the same as that of the liquid in mass, and to compare the number so obtained with the thickness given by a direct optical measurement based on the colour. If the ratio of the electrical thickness to the optical thickness is unity there is no reason to suspect a change in the specific conductivity. If it differs much from unity the presumption is in favour of such a change. One film, formed of a solution containing one part of oleate of soda to 60 of water without the addition of any metallic salt, which was observed on July 7, 1892, lasted two hours and a half. During this

time it thinned to the white of the first order, was thickened by sending a current up it, and was again allowed to become thin. The following table gives the optical thickness and the ratio of the electrical to the optical thickness. It will be observed that the latter differs considerably from unity, and increases as the film becomes thinner.

TABLE XIV.

Optical thickness in $\mu.\mu.$	Ratio of electrical to optical, <i>i.e.</i> , to true thickness.
641	1.66
484	1.69
388	1.60
332	1.81
320	1.78
314	2.07
"	1.90
307	1.84
296	1.98

The electrical thickness was also measured on each occasion when the film displayed the white of the first order. Another film was then formed, and after its thickness had been very rapidly reduced by means of a current, the electrical thickness of the white was again determined. The numbers thus obtained were 407, 430, and 465 $\mu.\mu.$ respectively, the mean being 434 $\mu.\mu.$ As the true thickness corresponding to this colour is 97 $\mu.\mu.$, it will be seen that the ratio is 4.47.

Summing up we have the results given in the following Table.

TABLE XV.—Solution of oleate of soda containing 1 part of oleate in 60 of water, but no metallic salt.

Colour.	Optical, <i>i.e.</i> , true thickness, in $\mu.\mu.$	Ratio of electrical to optical thickness.
Green of fourth order G (4, 1) .	641	1.66
Green of second order G (2, 1) .	296	1.98
White of first order	97	4.47
Black	27.7	5.8

The optical thickness assumed for the black is the mean of those obtained from films of similar constitution (see Tables IV. and VII.), the electrical thickness, viz., 160 $\mu.\mu.$, is deduced from the value obtained for films containing 1 part of soap to 40 and 70 of water respectively.

It is important to remember that after the white had been exhibited, the film was thickened and then allowed to thin to the white again, and that the ratio of the electrical and optical thicknesses changed from a large to a relatively small, and then again to a large value. This is shown below.

TABLE XVI.

Time.	Colour.	Optical thickness.	Ratio.
h. m. s.			
3 16 0	Yellow of the second order Y (2, 0). .	320	1.78
3 17 45	Green of the second order G (2, 3) . .	301	1.84
Later	White of the first order	97	4.19
4 23 15	Red of the second order after the film had been thickened	388	1.60
4 49 0	White of the first order	97	4.47

The numbers given in this Table, combined with the fact that we always get a much larger ratio (of which the mean is 5.8), when the film is thin enough to display the black, are certainly consistent with the view than when the same colour is reproduced, the ratio is, at all events, approximately the same, and that, therefore, the change in specific conductivity indicated by the value of the ratio is a function of the thickness. The connection is further illustrated by the curve on p. 526.

We now proceed to consider films formed of liquid, to which a metallic salt has been added.

The following Table gives the values of the ratios of the electrical and optical thickness as obtained from a number of different films. The numbers are arranged in such a way as to bring out the various points which are worth attention.

TABLE XVII.

Solutions containing 3 per cent. of KNO_3 but no glycerine.			
Number of film.	Date.	Optical, <i>i.e.</i> , true thickness.	Ratio of electrical to optical thickness.
Film 2	1892. July 11	662	1.06
		563	1.07
„ 2	„ 12	600	1.03
		545	1.00
		528	0.94
		496	0.93
		429	1.08
		412	1.15
		337	1.24
		305	1.21
		253	1.16
„ 3	„ 11	320	1.28
		300	1.14
		289	1.12
„ 4	„ 11	401	1.22
		307	1.25
		305	1.27
		215	1.25

In the first place it will be noticed that in all cases the ratio is much less than when no salt is added to the solution. At optical thicknesses above $450\ \mu.\mu.$, the number varies on each side of unity, giving no evidence of a change in specific conductivity. This is proved by the films numbered 2, on July 11 and 12. At thicknesses between 200 and $450\ \mu.\mu.$, the ratio is generally above unity, being in some cases as large as 1.27 or 1.28 . It is, however, to be observed that there is no clear indication of an increase in the ratio as the film thins. The value corresponding to the smallest optical thickness is not the greatest in the cases of film 2, July 12, and film 4, July 11, and is actually the least of those furnished by measurements on film 3, July 11.

The optical and electrical measurements of the thickness of black films formed of a 3 per cent. solution are in as close accord as the nature of the experiments will permit, the electrical being as a matter of fact rather the smaller of the two. Thus, from Tables VII. and I., we get $10.6\ \mu.\mu.$, and $12.4\ \mu.\mu.$, for the mean electrical and optical thicknesses respectively. The discrepancies between the individual experiments are too great to enable us to insist on the accuracy of this difference, but it is evident that there is no such striking divergence between the results of the two methods as is remarked when no salt is present.

We have tried from time to time to obtain some measures of the electrical thickness of films formed of a solution containing 3 per cent. KNO_3 , at thicknesses intermediate between that corresponding to the black and $200\ \mu.\mu.$ Such observations would be very valuable in helping us to decide whether there is or is not a real maximum of specific conductivity at about $100\ \mu.\mu.$, which is suggested by the fact that (in spite of the discrepancies above noted) the ratio of the electrical to the optical thickness is less for thick films and for black films than for those whose thicknesses lie between $200\ \mu.\mu.$, and $400\ \mu.\mu.$ Unfortunately, though we have exhausted every device known to us, sometimes leaving the film to thin unaided, sometimes passing weak and sometimes strong currents through it, we have never succeeded in getting the white of the first order. This connecting link cannot, therefore, be at present supplied, but the facts are sufficient to justify the proposition that the increase in specific conductivity observed in the case of an unsalted solution is largely diminished by the addition of a salt. It is indeed open to question whether the evidence would not support the statement that there is no appreciable change in the specific conductivity of a film containing 3 per cent. of salt, but although we hardly feel justified in drawing this general conclusion, there can be no doubt whatever that it is true for a *liquide glycérique* for the black on the one hand, and for thicknesses greater than $374\ \mu.\mu.$ on the other, and therefore, in all probability (though not quite certainly) for intermediate thicknesses. This conclusion rests upon our previous work. In 1881 we proved that there is no change in the specific resistance of a film of salted *liquide glycérique* down to a thickness of $374\ \mu.\mu.$ ('Phil. Trans.,' Part 2, 1881, p. 447, *et seq.*) while the optical and electrical thicknesses of black films are 10.7

and $11.9 \mu.\mu.$, respectively ('Phil. Trans.,' 1883, Part 2, p. 661). Both of these conclusions have been verified by more recent experiments. In the following table we give the ratios of the electrical to the optical thicknesses found in the case of two films observed on Jan. 9, 1892, which are in entire agreement with our 1881 observations on thick films.

TABLE XVIII.

Optical thickness in $\mu.\mu.$	Ratio of electrical to optical thickness.	
	Film I.	Film II.
789	0.996	
735	1.012	
732		1.064
711		1.022
708	0.989	
672	1.012	
661		1.045
631		1.052
627	1.014	
618		1.023
611		1.005
585	0.995	

Taking the means of these values and making the proper corrections for temperature we get

Specific resistance of liquid in mass	142.6 ohms. per cub. centim.
„ „ from Film I.	142.0 „ „
„ „ from Film II.	138.0 „ „

On referring to page 479 of our paper of 1881 it will be seen that the agreement here obtained is as good as that on which our former conclusions are based.

The thickness of black films formed of salted *liquide glycérique* has also been measured again and again, with the result that the accuracy of our 1883 measurements has in every case been confirmed.

Preliminary Discussion of the Results.

Up to this point we have as far as possible confined our attention to experiment. We now propose to give our reasons for postponing any full discussion of the possible causes of the phenomena we have observed.

The most probable directions in which to look for an explanation are in the formation of a pellicle of different conductivity from the interior, or in a change in the conductivity due to the direct action of the surface forces as the film becomes thin, or in a combination of both.

If we assume that the film consists of two surface layers and an interior, which can

be sharply distinguished from each other, and whose properties are different, it is easy to express the relation between the optical and electrical thicknesses by a formula.

Let T and x be the total thickness and the thickness of a surface layer of the film respectively.

Let K , k , and κ be the conductivities of the liquid in bulk, of the interior of the film, and of the surface layer respectively.

Then if T_e be the thickness deduced from a measurement of the resistance we have, if

$$T > 2x,$$

$$r = \frac{T_e}{T} = \frac{(T - 2x)k + 2x\kappa}{TK}.$$

Hence

$$T_e = \frac{Tk}{K} + \frac{2x(\kappa - k)}{K}.$$

If, now, the results of the experiments be plotted with T_e and T for ordinate and abscissa respectively, the formula shows that—

- (1.) If the film be of constant conductivity equal to that of the liquid in bulk, the results will be represented by a straight line through the origin inclined at 45° to the axes. This follows from the assumption $K = k = \kappa$.
- (2.) If the conductivity be constant throughout the film, but different from that of the liquid in bulk, the line will pass through the origin, but will not be inclined at 45° to the axes.

In this case $K \neq k$ and $k = \kappa$.

- (3.) If the conductivity of the surface layers be different from that of the interior $\kappa \neq k$, and the line will not pass through the origin.
- (4.) If the conductivity of the interior be variable, and if k can be expressed by a formula of the type

$$k = k_0 + \frac{A}{T^n} + \&c.,$$

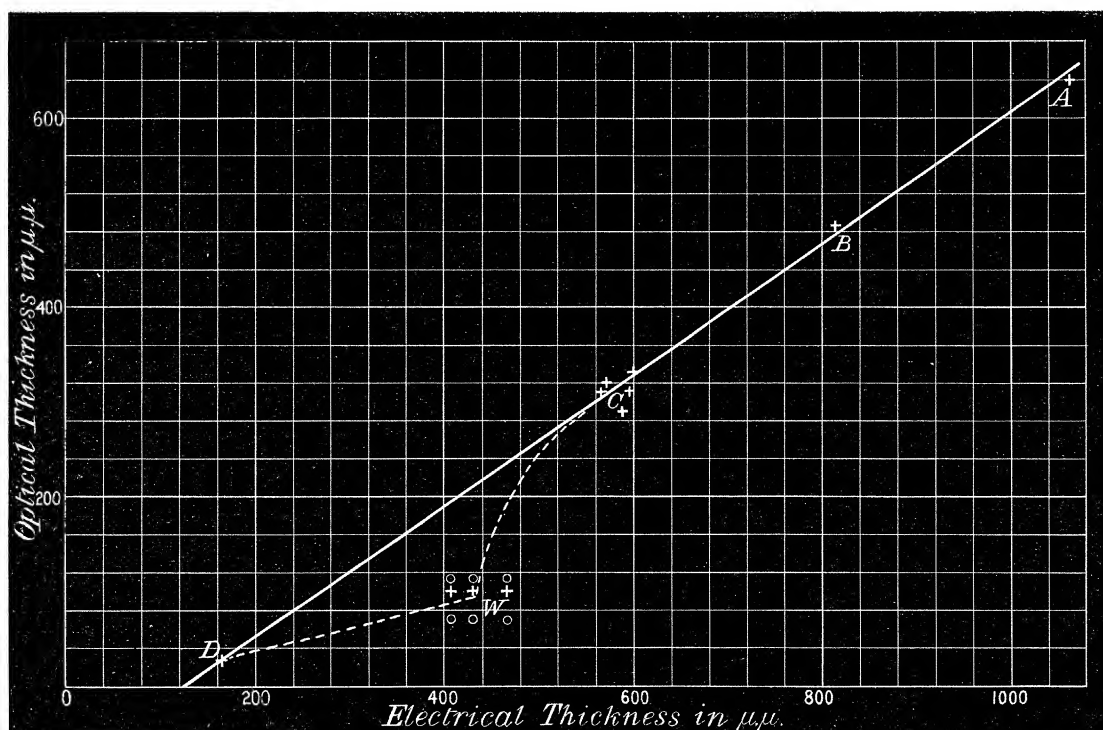
the expression becomes

$$T_e = \frac{Tk_0}{K} + 2x \frac{(\kappa - k_0)}{K} + \frac{T - 2x}{K} \frac{A}{T^n} + \&c.$$

All terms similar to that in which A occurs vanish when $T = 2x$. Hence if n be large, the term in T^n will be small when T is large, and will vanish when $T = 2x$. Thus a straight line will pass through the points corresponding to large values of T and through the point corresponding to $T = 2x$. For intermediate values the points given by the observations will not lie on the line in question.

The accompanying diagram shows how far our observations can be made to accord with these theories.

The point D is determined from the mean optical and electrical thicknesses of the black. It must, however, be remembered that we have every reason to believe that there are two thicknesses corresponding to this tint, and that unless the conductivity and the thickness are connected by a linear relation, the mean thickness of a large number of films will not necessarily correspond to their mean conductivity.



The three crosses at W correspond to the three electrical thicknesses of the white obtained by different observations. The optical thickness is assumed to be 100 $\mu\mu$. The circles indicate the extreme errors which could be due to errors in colour estimation. The other observations represented by A and B, and the group represented by C, do not require special remark. The principal deductions which can be made from these observations are as follows :—

- (1.) The points do not lie on a straight line inclined at 45° to the axes. Hence the conductivity of the interior of the film is different from that of the liquid in mass.
- (2.) The points A, B, D, and the centre of the group C, lie nearly on a straight line. If, therefore, we waive the objection above pointed out with regard to D, and note the fact that the group W certainly does not lie on this line, the facts are consistent with the theory that the film consists of an interior

of different conductivity from the liquid in mass, bounded by pellicles of different conductivity from itself, and that when it becomes thin (about 300 $\mu\mu$), new forces (presumably surface forces) modify the conductivity in a way which can be approximately represented by supposing that the conductivity of the interior alone alters.

We do not, however, at present wish to draw from these observations any but two conclusions :—

- (1) The theory of the formation of a pellicle of different conductivity from the rest of the film will not by itself explain all the facts.
- (2) Something in the nature of a discontinuity appears to occur at a thickness of about 100 $\mu\mu$, which is but little greater than that which we have already fixed as the upper limit of the range of unstable thicknesses to which we attribute the discontinuity at the edge of the black part of a film.

On the whole, then, we think it most likely that the changes observed at the smaller thickness are in part at all events due to the direct action of the surface forces, but that their action is complicated by some cause which at greater thicknesses forms a pellicle and also affects the interior of the film.

There is indeed a great deal of evidence for the fact that if the surface of a solution of soap in water has been long exposed a pellicle is formed upon it. The surface tension of such a solution is about one-third of that of pure water, but Lord RAYLEIGH has shown that there is no measurable difference if the surface of the solution has only been formed for a very small portion of a second. It is obvious, therefore, that the surface of a solution of soap in water is modified when exposed to the air.

We, on the other hand, have proved ('Phil. Trans.,' 177, Part 2, 1886, p. 659) that every disturbance of the surface of a soap film increases its surface tension, and that the normal value proper to what may be called an *aged* surface is not regained for several minutes.

In this respect the variations of surface tension and of electrical conductivity behave similarly. Both are affected when the film is disturbed by the passage of an electrical current.

On referring to Table XIV. we observe that two of the values of the ratio of the electrical to the true thickness (r), viz., those which correspond to the thicknesses 388 and 314 $\mu\mu$, respectively, are inconsistent with the others.

If the table is rearranged in the order in which the experiments were performed, these facts gain significance. The exact sequence of events was as follows :—

Current from 20 cells sent down the film before the measurement was made :

$$(1) \text{ T (true thickness) } = 641 \mu\mu, r = 1.66.$$

Current from 20 cells sent up the film :

(2) T = 484 $\mu.\mu.$	$r = 1.69,$
332 „	1.81,
314 „	1.90,
White	4.19.

Current sent up and down the film in turn :

(3) T = 320 $\mu.\mu.$	$r = 1.78,$
307 „	1.84,
296 „	1.98.

Film began to thicken spontaneously :

(4) T = 314 $\mu.\mu.$	$r = 2.07.$
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An upward current was next applied and the film allowed to thin with the following results :

(5) T = 388 $\mu.\mu.$	$r = 1.60.$
White	$r = 4.47.$

It will be noticed that every time the film was disturbed the value of r fell, *i.e.*, the specific conductivity of the film was reduced more nearly to that of the liquid in mass, nor was this merely due to the fact that the first effect of the currents was in every case to thicken the film, the value of r corresponding to a given thickness was always less in a more recently disturbed film. This is proved by comparing the values of r corresponding to 320 $\mu.\mu.$ in groups (3) and (2), and those corresponding to 388 $\mu.\mu.$ in groups (5) and (2).

We take it that this is sufficient proof that though the phenomenon we are studying depends on the thickness, it is not merely an explicit function of the thickness of the film, *i.e.*, is not due exclusively to a peculiar molecular constitution depending on the thickness. If this were so, the molecular conditions peculiar to a particular thickness would be immediately re-established as soon as the film regained that thickness after disturbance.

We think that the next step should be to try to separate the effects due to the pellicle and to the capillary forces if both co-exist. The pellicle is possibly due to chemical actions between the liquid and the atmosphere. An apparatus is in course of construction which will enable us to experiment in other gases more satisfactorily than hitherto. For the moment we venture to lay our results before the Society without a full explanation.

We believe that the main fact, *viz.*, the change in the conductivity of an unsalted

soap film is entirely new. We hope that the observations which we have made on it will be of interest.

It is difficult to assign a reason why the addition of salt to the liquid should produce so great a change in the results. In part, the better conducting salt probably masks effects which when soap alone is used become predominant, but we think it likely that in part at all events it actually prevents the changes to which the change of conductivity is due.

However this may be, we venture to think that there can be no doubt as to the facts that whereas the conductivity of a thin unsalted soap film is considerably greater than that of the liquid in bulk, the difference is so reduced in the case of a salted film with or without the addition of glycerine that the mean thickness of a number of black films whether measured electrically or optically is the same to within the limits of the error of experiment.